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(54) IMPROVED ALUMINUM-ZIRCONIUM AEROSOL ANTIPERSPIRANT COMPOSITION AND PROCESS

(71) We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an antiperspirant; and more particularly is concerned with aerosol antiperspirant powder spray compositions containing a powder antiperspirant active complex.

Antiperspirant compositions in the form of aqueous creams, lotions, sticks, and roll-ons have been known in the art for many years. More recently, aerosols under pressure have become popular as a convenient form for application to the skin. Most preferred of the aerosol compositions are those in which the antiperspirant active is suspended as a dry, impalpable powder in a nonaqueous medium, chiefly propellant. Such compositions apply the active antiperspirant salt to the skin effectively and feel dry, smooth and comfortable. Furthermore, because the antiperspirant compound is suspended rather than being dissolved in a liquid, it is less corrosive and can be used in lined cans. Such powder compositions are further advantageous in that they are generally less irritating to the skin.

Typically, such a powder aerosol composition contains one or more metallic, acidic astringent salts as the antiperspirant active; i.e., for perspiration control. In addition, a suspending agent is employed to keep the antiperspirant compound from agglomerating or settling out and packing tightly at the bottom of the aerosol container. A carrier liquid is added so that the stream issuing from the aerosol container is a moist spray which effec-

tively adheres to the skin instead of a dusty cloud which does not adhere as well. A propellant is added to force are antiperspirant composition out of the container. Minor adjuncts such as antimicrobial compounds and perfumes are optional.

U.S. Patent 2,906,668 discloses the preparation of an aluminum hydroxychloride/zirconium oxychloride complex by a process of heating and mixing which results in the immediate formation of a gel.

Another pertinent patent is U.S. Patent 2,814,585 which discloses an aqueous antiperspirant composition, the preferred embodiments of which include zirconyl chloride (zirconium oxychloride), aluminum chlorhydroxide (ACH) and glycine. A later patent, U.S. 2,854,382, discloses that zirconyl hydroxy chloride is preferred over zirconyl chloride. Both of these references are directed primarily toward the use of the active ingredients dissolved in a liquid non-aerosol composition.

In addition to the above prior art, U.S. Patent 3,288,681, British Patent Specification No. 1,167,173; and British Patent 987,301 disclose various powder aerosol systems.

Accordingly, it is an object of the present invention to provide an advantageous, homogeneous powder antiperspirant complex having a higher pH (for the same Zr level as other materials) thereby being less corrosive and less irritating in nature.

It is also an object of the present invention to provide an effective antiperspirant complex without having any extraneous materials present.

It is another object of the present invention to provide a highly efficient antiperspirant complex for incorporation into various compositions at significantly lower concentrations thereby providing significant economic advantages.

It is yet another object of the present inven-

tion to provide highly efficacious, comfortable and convenient powder antiperspirant aerosol compositions for application to the skin.

It is still another object of the present invention to provide a convenient and economical process for the preparation of said antiperspirant powder complex,

These objects which will become apparent are further defined in the disclosures hereinafter.

It has been discovered that a highly effective antiperspirant complex is formed by a process comprising the steps of:

- (A) Heating an aqueous solution containing from 1 to 3.2 parts by weight of aluminium chlorhydroxide to a temperature of from 190°F to 225°F;
- (B) Adding an aqueous solution containing 1 part by weight of zirconyl hydroxychloride to the aluminium chlorhydroxide solution at such a rate that the addition takes from 2 hours to 5 hours, while heating and agitating, the total anhydrous solids content when all the zirconyl hydroxychloride has been added being at least 10% by weight; and
- (C) Heating and agitating the aluminium chlorhydroxide - zirconyl hydroxychloride mixture at from 190°F to 225°F for from $\frac{1}{2}$ hour to about 5 hours until a stable complex forms.

The process defined above inevitably produces a stable complex. The course of the reaction is conveniently monitored by the viscosity of mix, the reaction being complete when no further reduction in viscosity takes place.

In addition to the above process, it has been discovered that the resultant aqueous complex of step (C) can be dried to an impalpable complex for incorporation into aerosol compositions by a process which comprises the additional steps of:

- (D) Drying the resultant mixture at a temperature of from 100°C to 230°C to a moisture level of from 1% to 15% by weight; and
- (B) Comminuting the resultant dried powder complex into the form of an impalpable powder.

It has also been discovered that the dry antiperspirant complex formed by the above process can be incorporated into aerosol compositions which comprise:

- (A) From 1% to 12% by weight of a powder antiperspirant complex as formed above;
- (B) From 0.1% to 5% by weight of a suspending agent;
- (C) From 1% to 15% by weight of a carrier liquid of low volatility; and
- (D) An anhydrous liquefiable gas propellant in an amount sufficient to produce an aerosol spray.

The preferred complex of this invention is prepared by heating an aqueous solution containing 1.6 parts by weight of aluminium chlorhydroxide (50% by weight nominal concentration) to a temperature of about 190°F; adding an aqueous solution containing 1 part by weight of zirconyl hydroxychloride (33—1/3% by weight nominal concentration) slowly over a period of about 3 hours to the aluminium chlorhydroxide solution while maintaining heating and agitation; continuing heating and agitation for 3 hours; and; then cooling to ambient temperature. The complex is then dried in trays at 140°C for 24 hours and comminuted by ball milling and screening. The term "nominal concentration" used herein in all cases refers to anhydrous solids. It is meant to convey that the materials to which it refers are purchased as aqueous solutions stated to have certain concentrations. The actual concentration may vary very slightly from the stated concentration or "nominal concentration".

Preferably, the level of solid complex in water is from 10% to 60% by weight; more preferably from 30% by weight to 50% by weight; and most preferably about 40% by weight.

Examples of satisfactory drying means include ordinary oven drying, spray drying, drum drying, vacuum drying or microwave drying.

Examples of suitable comminution processes include ball milling, roller milling, passing through a colloidal mill, jet impact mill, or other suitable means,

Depending upon the type of comminution equipment utilized, it may be necessary to pass the comminuted powder through a sieve to further achieve uniformity and eliminate oversize.

The particle size of the antiperspirant complex should be small enough such that an even spray is achieved and nozzle and valve malfunction are avoided. A particle size of about 100 microns in diameter is suitable with the preferred size being from 10 microns to about 25 microns in diameter. The result is a highly effective, relatively non-corrosive and essentially non-irritating antiperspirant powder complex for incorporation into a variety of powder aerosol compositions for use on the skin.

It has been surprisingly found that an antiperspirant complex having superior characteristics and properties is formed by steps A—C of the process recited above.

More specifically, it has been found that utilizing the process of the present invention results in the production of an antiperspirant having a higher pH than complexes formed by processes of the prior art, e.g., U.S. 2,906,668 for the same Al/Zr ratio. A complex with a pH of from about 3.0 to about 3.6 (when added to water) is achieved by the process of

the instant invention. pH is significant in the antiperspirant art. The lower pH's of the products (in water) obtained by some processes of the prior art necessitate the addition of buffering agents and anti-gelling agents to reduce skin irritation, fabric destruction and package corrosion. In addition, the presence of buffering and anti-gelling agents necessitates the use of compatibilizers. The use of compatibilizers is believed to cause problems of valve clogging, fabric staining, and skin irritation in addition to adding to the cost of the final product.

The process of the present invention results in the production of a higher pH antiperspirant complex which is less irritating to the skin, less damaging to fabrics, and less corrosive to packaging. The complex also eliminates the need for the addition of buffering, anti-gelling and compatibilizer agents.

The process of the present invention (steps A—C) also results in the formation of a liquid antiperspirant complex rather than a gel. This is significant, as said liquid complex can be readily dried as disclosed in steps D—E to an impalpable powder complex for incorporation into a variety of powder aerosol compositions.

Powder aerosol antiperspirant compositions as hereinbefore described can be prepared using the complex of this invention as set forth in detail hereinafter.

Component A

For the purpose of the present invention, the antiperspirant compound is the powder complex which has been described in detail heretofore. Between 1% and 12% by weight, preferably 2.5% to 6% by weight incorporated into an aerosol composition has been found to give superior antiperspirant effectiveness. Below about 2%, the antiperspirant effectiveness falls off. Above 12% is not practical because the antiperspirant effectiveness does not increase commensurate with additional quantities used; in addition to causing handling and atomization problems.

Component B

The suspending agent keeps the powder antiperspirant complex in suspension within the composition. Although some settling may occur, the antiperspirant complex remains in a readily redispersible state. Suitable suspending agents include a colloidal silica of a particle size below .03 microns. Colloid silica as disclosed in British Patent Specification No. 1,167,173 is available commercially as Cab-O-Sil M-5 (Trade Mark), a submicroscopic particulated pyrogenic silica. Another suitable suspending agent for the invention is a hydrophobic clay which is the reaction product of clay e.g. bentonite and a quaternary ammonium surfactant preferably dimethyldistearylammonium chloride. Such a hydrophobic clay is available commercially as Bentone 38 (Trade Mark). Fumed alumina Al_2O_3 can also be used.

Primary aliphatic amines of from C_{12} — C_{20} are also available. Examples of such compounds include lauryl amine, tetradecyl amine, hexadecyl amine, octadecanoyl amine, and eicosyl amine. Still other suitable suspending agents are aliphatic monoalkylol amides having a fatty acid carbon chain of from about C_{12} — C_{20} , and 2 or 3 carbon atoms in the alkylol chain as disclosed in British co-pending No. 61117/70 (Serial No. 1329159). Examples include coconut monoethanol amide and octadecanoyl monoethanol amide.

Any of the suspending agents described above can be used in amounts of from 0.1% to 5% by weight. Amounts of suspending agents of from 0.3% to 0.8% are preferred. The especially preferred suspending agent for the purpose of this invention is Bentone 38.

Component C

A carrier liquid of low volatility is used in the invention so that the stream issuing from the aerosol container is a moist spray rather than a gritty, dusty cloud. This imparts a cosmetic feeling to the skin when applied thereto and reduces the likelihood of breathing the otherwise dry powder. The carrier liquid also aids efficacy by keeping the antiperspirant compound in contact with the skin so that it does not flake off or wash off. Thus, the carrier liquid is needed for the practical use of the invention. Examples are carboxylic esters like isopropyl myristate and isopropyl palmitate; hydrocarbons like mineral oil and tetradecane; alcohols such as lauryl alcohol, hexadecyl alcohol, and oleyl alcohol; carboxylic acids such as lauric and oleic acid; lanolin and its derivatives such as acetylated lanolin; and silicone oils such as dimethylpolysiloxane. Other operable carrier liquids are more hydrophilic than the above-mentioned compounds, for example, organic compounds containing multiple ester groups. This includes, but is not limited to, diesters of dibasic organic acids. Examples of compounds containing multiple ester groups that are suitable for the instant invention are di-n-octyl-n-decyl phthalate, di-n-octyl phthalate, di-n-hexyl phthalate, di-n-butyl phthalate, diethyl sebacate, diisopropyl adipate, and ethyl ethylcarboxymethyl phthalate

[ortho $C_2H_5OOC-\phi-COOCH_2COOC_2H_5$].

Still other operable carrier liquids are even more hydrophilic than these esters. Among them are polyethylene glycol monolaurate and butoxy-polyoxyethylene oxypropylene glycols [the Ucon 50 HB series: Trade Mark—Union Carbide].

Among these various carrier liquids, carboxylic esters having from about 12 to about 26 carbon atoms are preferred. As described supra, they can be either aliphatic or aromatic and can contain either one ester group or multiple ester groups. Especially preferred are di-n-butyl phthalate, diethyl sebacate, diisopropyl

adipate, and ethyl ethylcarbomethyl phthalate.

Any of the carrier liquids described above can be used in amounts from 1% to 15%. Below about 2% the carrier liquid is insufficient to form a moist spray and the spray is, therefore, undesirably dusty and gritty and does not adhere well to the skin. Above about 15% the composition deposited upon the skin feels undesirably oily and greasy. Amounts of carrier liquid from 6% to 10% are preferred.

Component D

The propellant gas of the invention can be any liquefiable gas conventionally used for aerosol containers. Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, propane, butane, and isobutane, used singly or admixed. Trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, and isobutane, used singly or admixed, are preferred.

The amount of the propellant gas is governed by normal factors as well known in the aerosol art. It is satisfactory to consider the propellant as constituting the balance of the composition of the instant invention that is not accounted by the other components as detailed herein. The preferred limits of propellant are therefore from 70.7% to 93.9% by weight. Especially preferred limits are from 80% to 92%.

It will be understood that other ingredients may be added to the above composition in minor proportions without affecting the nature of the invention. An example of such an additional ingredient is perfume used in amounts from 0% to 0.8% by weight. Another example is the addition of an antimicrobial compound such as hexachlorophene, trichlorocarbonyl, trifluoromethylcarbanilide, 2,4,4'-trichloro-2'-hydroxy diphenyl ether or tribromosalicylanilide, which, when added in amounts of from 0% to 0.5% by weight, inhibit bacterial action upon perspiration and reduce odors resulting therefrom.

The following examples are submitted to further illustrate, but in no way limit this invention.

Example I further illustrates the method for the production of the powder antiperspirant active complex. Examples II through VIII further illustrate various aerosol compositions embodying the powder antiperspirant active complex and method for their preparation. In addition to Examples II through VIII, other suitable compositions into which the antiperspirant powder complex of the present invention can be embodied as the active component are found in British Patent Application No. 61117/70 (Serial No. 1329159); U.S. Patents 2,236,387, 3,288,681 and 2,405,153; British Patent 987,301 and British Patent Specification No. 1,167,173.

All parts, ratios, and percentages herein are by weight unless otherwise specified.

Example 1.

A process for the preparation of the powder antiperspirant complex of the present invention is as follows:

155 grams of a solution (50% nominal concentration) of aluminum chlorhydroxide (ACH) in water is heated in a suitable container to raise the temperature to 190°F. (The solution is agitated during the heating, utilizing suitable agitation means). About 1/3 of 138 grams of a solution (33-1/3 nominal concentration) of zirconyl hydroxychloride (ZCH) in water is then added in bulk to the ACH solution; and the remainder of the ZHC solution is added to the ACH solution in small portions over a period of 3 hours, the heating and agitation being continued during this period, and for about 3 hours after all the ZHC has been added. The heating and agitation is then stopped and the resulting aqueous complex (40% nominal concentration) is allowed to cool. The aqueous solution is subsequently dried in an oven at a temperature of 140°C. until a moisture content of about 5% is attained. The dried solution, now in a solid state, is then placed into a ball mill and milled for about 4 hours, giving a fine powder. The powder is then passed through a 325 mesh screen (ie. a Tyler screen having a mesh size of 44 microns) to obtain a uniform size product. The result is a powder antiperspirant active complex for incorporation into an aerosol composition.

Example II.

The following components are used to prepare an aerosol antiperspirant powder spray:

Component	Percent by Weight	
ZA ¹	3.50	
Isopropyl Myristate	8.00	
Bentone 38	0.60	
95% Ethyl alcohol	0.27	
Hexachlorophene	0.10	
Perfume	0.40	
Propellant ²	q.s. 100%	

1. Zirconyl hydroxychloride / aluminum hydroxychloride antiperspirant powder complex as prepared in Example I.

2. Selected from the following:

CCl₃F (stabilized): CCl₂F₂ (60:40)

CCl₃ (stabilized): CCl₂F₂:isobutane (48:32:20)

CCl₃F (stabilized): CCl₂F₂:CClF₂:CClF₂: n-butane (20:10:50:20)

45.5 grams of hexachlorophene is dissolved in 8.0 pounds of isopropyl myristate using a high speed mixer at a temperature of about

70°F. 3.5 pounds of the ZA active powder complex is then added to the batch and mixed for about 5 minutes at a temperature of 70°F. The ethanol (95%) is then added to the mixture and mixed for about 10 minutes at the 70°F. temperature. While the mixing continues, the temperature is slowly increased (2—3°F. 1 min.) until a temperature of from about 130°—150°F. is attained. The mixture is subsequently cooled to a temperature of about 110°F. while the mixing continues. The perfume is now added. The mixing is continued at a temperature of from 100°F. to 110°F. until the mixture becomes homogeneous. The mixture is allowed to cool to about 75°F. and is subsequently charged into an aerosol container. The propellant is then

added to the container using an under-the-cap filler.

The result is a highly effective powder aerosol antiperspirant composition for use on the skin.

The same process is used to prepare compositions identical to the foregoing except that different kinds of propellants are used as shown in the following table. In each case the general properties and the antiperspirant effectiveness of the composition when applied to the skin are substantially the same as that discussed above. Substantially equivalent results are obtained when different methods of product packaging, e.g., cold filling, pressure filling, and burrette filling, are used.

**% By Weight on a Propellant Basis
(100% propellant is equivalent to 87.5% of the composition)**

[illegible]

Example III.				
	Component	Percent by Weight		
	ZA ¹	3.50	1. Zirconyl hydroxychloride / aluminum chlorhydroxide antiperspirant powder complex prepared substantially as disclosed in Example I.	40
	Isopropyl myristate	8.00	2. CCl ₃ F: CCl ₂ F: butane (40: 30: 30) by weight	
5	Cab-O-Sil (M-5 or H-5)	0.60		
	Hexachlorophene	0.10		
	Perfume	0.40		
	Propellant ²	q.s. 100%		
	A highly effective aerosol powder antiperspirant spray results.			
10	1. Zirconyl hydroxychloride aluminum chlorhydroxide powder antiperspirant active prepared as disclosed in Example I.		Compositions identical to those disclosed in Example IV are prepared except that dibutyl phthalate is replaced by isopropyl myristate, isopropyl palmitate, mineral oil, tetradecane, lauryl alcohol, hexadecyl alcohol, oleyl alcohol, lauric acid oleic acid, lanolin, acetylated lanolin, dimethylpolysiloxane, di-n-octyl-n-decyl phthalate, di-n-octyl phthalate, di-n-hexyl phthalate, diethyl sebacate, diisopropyl adipate, and ethyl ethylcarboxymethyl phthalate [ortho C ₂ H ₅ OOCC—O—COOCH ₂ COOC ₂ H ₅]. Said compositions are prepared by a procedure substantially as disclosed in Example II. Results substantially equivalent to those obtained in Example IV are obtained in each case.	45
	2. CCl ₃ F: CCl ₂ F ₂ (60/40) by weight			
15	When dispensed from an aerosol container, a dry highly effective antiperspirant powder forms on the skin.			50
	Compositions identical to the foregoing in Example III are prepared as disclosed in Example II, except that hexachlorophene is replaced with trichlorocarbaniide, trifluoromethyl carbaniide, tribromosalicylanide and 2,4,4'-trichloro-2'-hydroxydiphenyl ether. The results are substantially equivalent to those obtained in Example II.			
20				55
	Example IV.			
25	The following components are used to prepare an aerosol antiperspirant powder spray, utilizing the procedures disclosed in Example II.			
	Component	Percent by Weight	Compositions identical to those disclosed in Example IV are prepared except that octadecanoyl monoethanol amide is replaced by Cab-O-Sil M-5, Bentone 38, lauryl amine, tetradecyl amine, hexadecyl amine, octadecyl amine, eicosyl amine, coconut monoethanol amide and octadecanoyl monoethanol amide. Said compositions are prepared utilizing procedures disclosed in Example II. Equivalent results to those obtained in Example IV are obtained in each case.	60
30	ZA ¹	3.50		
	Dibutyl phthalate	8.00		
	Octadecanoyl monoethanol amide	0.60		
35	Trichlorocarbaniide	0.10		65
	Perfume	0.40		
	Propellant ²	q.s. 100%		70

Examples V—VIII

Component	V	VI	VII	VIII
ZA ¹	3.50	3.50	3.50	3.50
Isopropyl myristate	8.00	8.00	8.00	—
Bentone 38	0.60	0.60	—	0.60
EtOH/H ₂ O 95.5% wt.	0.27	0.27	—	0.27
Trichlorocarbaniide	0.10	—	—	—
Geigy 3565 ²	—	0.10	—	—
Alon ³	—	—	0.60	—
Hexachlorophene	—	—	0.10	0.10
Dibutyl Phthalate	—	—	—	8.00
Perfume	0.40	0.40	0.40	0.40
Propellant ⁴ q.s.	100%	100%	100%	100%

¹Zirconyl hydroxychloride: aluminum chlorhydroxide — antiperspirant powder complex prepared substantially as disclosed in Example I.

²2,4,4',-trichloro-2'-hydroxydiphenyl ether.

³Fumed alumina (Al₂O₃)

⁴CCl₃F:CCl₂F₂ (60/40) by weight

Each of the above compositions is a highly effective dry aerosol powder antiperspirant for use on the skin.

WHAT WE CLAIM IS:—

1. A process for the preparation of antiperspirant complexes which comprises the steps of:

- (A) Heating an aqueous solution containing from 1 to 3.2 parts by weight of aluminium chlorhydroxide to a temperature of from 190°F to 225°F;
- (B) Adding an aqueous solution containing 1 part by weight of zirconyl hydroxychloride to the aluminium chlorhydroxide solution at such a rate that the addition takes from 2 to 5 hours, while heating and agitating, the total anhydrous solids content when all the zirconyl hydroxychloride has been added being at least 10% by weight; and
- (C) Heating and agitating the aluminium chlorhydroxide - zirconyl hydroxychloride mixture at a temperature of from 190°F to 225°F for from ½ hour to 5 hours until a stable complex forms.

2. The process of claim 1 wherein the total solids content at the end of step (B) is from 30% to 50%. 30

3. The antiperspirant complex prepared by the process of claim 1.

4. The process of preparing the complex of claim 1 in a dry, finely divided state which comprises the steps of (A), (B), and (C) and in addition: 35

(D) Drying the resultant mixture at a temperature of from 100°C. to 230°C. to a moisture level of from 1% to 15% by weight; and 40

(E) Communiting the resultant dried inorganic-organic antiperspirant complex into the form of an impalpable powder. 45

5. The powder antiperspirant complex prepared by the process of Claim 4.

6. The powder antiperspirant complex of Claim 4 wherein the ratio of aluminum chlorhydroxide to zirconyl hydroxychloride is about 1.6:1. 50

7. A powder aerosol antiperspirant composition for application to the skin which comprises:

- (A) From 1% to 12% by weight of the astringent powder antiperspirant complex of Claim 4.
- 5 (B) From 0.1% to 5% by weight of a suspending agent;
- (C) From 1% to 15% by weight of a carrier liquid of low volatility and
- 10 (D) A sufficient amount of an anhydrous gas propellant to produce an aerosol spray.
8. The powder aerosol antiperspirant composition of Claim 7 wherein the suspending agent is selected from colloidal silica, a reaction product of bentonite and dimethyldistearyl ammonium chloride, lauryl amine, tetradecyl amine, hexadecyl amine, octadecanoyl amine, coconut monoethanol amide and octadecanoyl monoethanol amide.
- 15 9. The powder aerosol antiperspirant composition of Claim 7 wherein the carrier liquid is selected from isopropyl myristate, isopropyl palmitate, di-n-butyl phthalate and diisopropyl adipate.
10. The composition of Claim 7 wherein the gas propellant is selected from trichloro- 25 fluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, nonochlorodifluoromethane, trichlorotrifluoroethane, propane, butane, isobutane and mixtures thereof.
11. The composition of Claim 7 wherein 30 present are components (A), (B), (C) and (D) and in addition:
- (E) From 0% to 0.5% by weight of an antimicrobial selected from trichloro- 35 carbanilide, hexachlorophene, trifluoromethyl carbanilide, tribromosalicylanide, and 2,4,4'-trichloro-2'-hydroxydiphenyl ether; and
- (F) From 0% to 0.8% by weight of per- 40 fume.

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